

First principle predictions of isotopic shifts in H₂O

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Abstract

We compute isotope independent first and second order corrections to the Born-Oppenheimer approximation for water and use them to predict isotopic shifts. For the diagonal correction, we use icMRCI wavefunctions and derivatives with respect to mass dependent internal coordinates to generate the mass independent correction functions. For the non-adiabatic correction, we use scaled SCF/CIS wave functions and a generalization of the Handy method to obtain mass independent correction functions. We find that including the non-adiabatic correction gives significantly improved results compared to just including the diagonal correction when the Born-Oppenheimer potential energy surface is optimized for H₂¹⁶O. The agreement with experimental results for deuterium and tritium containing isotopes is nearly as good as our best empirical correction, however the present correction is expected to be more reliable for higher, uncharacterized, levels.

I. INTRODUCTION

Starting with the work of Polyansky *et al.*,[1] empirical potential energy surfaces of water had reached a level of accuracy which enabled one to detect the need for mass dependent corrections arising from the breakdown of the Born-Oppenheimer approximation. The first attempt to predict the mass corrections was carried out by Zobov *et al.*[2], who calculated the diagonal (first order) correction at the SCF level. They used this with an *ab initio* PES and found some improvement, although the errors were still too large to be unambiguous. Subsequently we[3] determined an empirical PES which reproduced $\text{H}_2\text{ }^{16}\text{O}$ energy levels very well, but when we applied the Zobov *et al.* correction, we found that it did not predict the necessary isotopic shifts. Thus we determined an empirical mass dependent correction to our PES using data from HDO and D_2O , and this greatly improved the results for all the other isotopomers, however there remained discrepancies for the tritium isotopes, and because of the paucity of data for D_2O , this correction is only reliable for low lying levels.[3]

It would be most advantageous to the analysis and assignment of experimental spectra if reliable *ab initio* predictions of the mass dependent corrections is made available. This is because to a large extent, all of the information about the Born-Oppenheimer PES is contained in the results of a single isotopomer. Experimentally, it is much simpler to deal with a single isotopomer. For example, one can obtain essentially pure samples of H_2O and just obtain the spectrum of that species. However, it is not possible to obtain a pure sample of HDO, for collisions generate H_2O and D_2O as well, and so one has to deal with interfering H_2O and D_2O lines on top of the more complex spectrum that HDO has due to its lower symmetry. Molecules such as O_3 give rise to even more complicated mixtures of isotopomers. Analyzing and reliably assigning experimental spectra is a great deal of work. If theoreticians could reliably predict isotopic shifts, then that would be a much more efficient means of generating spectral data.

We compute the mass dependent corrections to the Born-Oppenheimer approximation using the second order perturbation theory result of Bunker and Moss[4] with *ab initio* wavefunctions to compute the required matrix elements.[5] The first order correction is a mass dependent correction to the PES, sometimes called the Born-Oppenheimer diagonal correction (BODC). The second order correction leads primarily to a mass dependent correction to the nuclear kinetic energy operator. This is usually called the non-adiabatic correction.

We have recently developed tools to compute these corrections and applied them to H₂O.[5] There we found that the SCF approximation used by Zobov to compute the first order correction is not reliable. In the present work we report predictions of isotopic shifts for deuterium and tritium containing isotopes using a newly optimized Born-Oppenheimer PES including non-adiabatic effects and a more accurate first order correction. We also derive a generalization of the Handy method for the diagonal correction to compute non-adiabatic correction functions from mass independent cartesian derivative matrix elements.

II. OPTIMIZING THE PES

In our previous work,[3] we obtained the empirical PES V^{emp} as

$$V^{emp} = c^{5Z} V^{5Z} + c^{core} \Delta V^{core} + c^{basis} \Delta V^{basis} + \Delta V^{rest}, \quad (1)$$

with c^{5Z} , c^{core} , c^{basis} , and the 18 parameters in ΔV^{rest} determined by a least squares fit to 5493 ro-vibrational transitions with $J \leq 5$. This calculation did not include any non-adiabatic effects. In the kinetic energy operator, we used the nuclear masses. For the first step in the present work, we re-optimize c^{5Z} , c^{core} , c^{basis} , and the 18 parameters in ΔV^{rest} including non-adiabatic effects. This produces the PES we call V^{nemp} .

The non-adiabatic corrections were obtained as an extension of our previous work.[5] Since the functional form used for the corrections does not extrapolate properly and in the present work we are considering higher energies, we extended our grid in R_1 and R_2 to 0.775-1.425 Å in steps of 0.05 Å, and Θ to 50 - 170 degrees in steps of 10 degrees, and the energy cut off was 20,000 cm⁻¹. We fit these (693 unique) 1292 points to the same polynomial as in our previous work. In these calculations, the ground electronic state is treated using the SCF method, the excited states by the singles CI method, and the results were scaled by 1.1. This scale factor was obtained by matching the computed and experimental rotational g factors.[5] We used the aug-cc-pVTZ basis.[6]

In our optimizations of the parameters in our PES, we use different experimental data than we used previously. In previous work we fit ro-vibrational transition energies. One problem with this is since ro-vibrational transition energies are differences in energy levels, it is hard to judge the amount of unique data one is fitting. Furthermore, there is the possibility of inconsistencies in ro-vibrational energies that make up the transition energies. So in the

present work, we use a different strategy. We start by compiling a list of ro-vibrational energies. These were determined as follows. We took the transition frequencies given in HITRAN 96,[7] and augmented this with the more recent data from the literature.[8-10] We then iteratively solved for ro-vibrational energies with respect to the zero point energy. This gave many estimates of the ro-vibrational energies, and we only retained consistent energies, which were defined as energies with at least 2 determinations, and a root-mean-square deviation from the average of the determinations less than 0.001 cm^{-1} . This resulted in a total of 1688 energy levels having J in the range $0 - 8$. In future work, we would use the compilation of Tennyson *et al.*[11] Now one desirable feature of our previous fit was that the errors had very weak dependence on J . To retain this feature, we weight rotational energies more than vibrational energies. We achieve this by organizing the ro-vibrational levels into groups which all have the same vibrational quantum number assignment. Then in each group, we subtracted the $J = 0$ energy from the higher J energies. If the $J = 0$ energy has not been determined, then the lowest J level that has been determined is used instead. In the fit then, there is a relatively small number of “purely” vibrational energies and a much large number of rotational energies. We fit these with equal weights.

For the present work we use a subset of the above data. This is to reduce the cost of the calculations and because we are not using hyperspherical coordinates.[3] We find our algorithm has difficulty converging highly excited states when we use r_1 and r_2 as coordinates.[5] Thus we consider only levels which correspond to roots 1-30 in a given JPS block. This results in a total of 1060 levels, of which 19 are “purely” vibrational levels and 1041 are rotational levels. We made our best attempt to ensure the proper matching of experimental and theoretical levels, but inadvertently some miss-assignments were made. We attempted to automatically detect these during the least squares process by computing the average absolute deviation from the average of the difference between the observed and calculated levels. We multiplied this by ten, and used this as a cut-off criterion to greatly diminish the weights for levels which had greater difference between the observed and calculated levels. In our final fit, 33 points were deleted by this rule, and the weighted root-mean-square (rms) error of the fit was 0.054 cm^{-1} . In this fit, we used the PES V^{emp} and the kinetic energy operator including non-adiabatic effects to generate the wavefunctions used as basis functions in the least squares fit.

In the course of this work, we also carried out optimizations not including non-adiabatic

effects for comparison. We found only slight changes to our previous PES,[3] and that the errors produced with and without non-adiabatic corrections were essentially the same. The only differences were in the values of the parameters. Of great interest was that when we included non-adiabatic effects, the optimum value of the parameters c^{basis} and c^{core} came out to be essentially unity, and so in the final fit, we constrained them to be unity. It should be noted that we did not include the BODC or relativistic corrections[12] to the PES in these optimizations. Initial trials including these corrections yielded essentially zero coefficients for the corrections. However, those calculations were carried out using the Zobov *et al.*[2] BODC, so if the calculations were repeated with the accurate BODC, this might not happen.

III. BODC

In Ref. 5, we reported calculations of the BODC of water using both CASSCF and SCF wavefunctions. For bending levels, the CASSCF and SCF results were very similar, but for the stretching levels, there were big differences. In the present work we have extended our capabilities and report the BODC computed at the icMRCI level, which should provide very accurate results. See Ref. 5 for the equations involved in the calculations. These calculations are carried out with a modified version of MOLPRO2000.1.[13] Two additional modifications were required to carry out these calculations. First of all, we had to extend the diabatic orbital scheme to perform rotations among the virtual orbitals. Secondly, we had to evaluate two-particle expectation values using the icMRCI wavefunction. This was achieved by modifying the CI code to perform a CI iteration using the converged wavefunction, but using different one and two-electron integrals. This is complicated by the fact that the two-electron repulsion integrals are symmetric with respect to interchanging the indices for the basis functions of one electron, while for the two-particle operators we require, the integrals are skew symmetric with respect to interchanging the indices. Nonetheless we have successfully made these changes.

When computing the BODC, one has three choices. One can use the Handy method, [14] which for a triatomic requires nine derivatives, six of which can be evaluated using C_s symmetry, and three which must be run in C_1 symmetry. Alternatively, one can carry out calculations using internal coordinates that depend on the isotopomer. For example, for Radau coordinates, this requires three derivatives and all the calculations can be run

using C_s symmetry.[5] Then the cost per point is less, but one has to perform additional calculations for each isotopomer of interest. Since in the present work we are interested in a large number of isotopomers, this would seem to favor the Handy method. However, avoiding the C_1 calculations can be a big advantage. We therefore seek economies by combining the methods. This is done as follows. We know that for isotopomer ABC, the Handy method gives the BODC as

$$\Delta V = \frac{1}{m_A}F_A + \frac{1}{m_B}F_B + \frac{1}{m_C}F_C, \quad (2)$$

where m_A is the mass of nuclei A , and F_A is the correction function of atom A , etc. If we knew the BODC for three linearly independent isotopomers, we can solve for the F_α , where α is A , B , or C . Specifically, we will carry out calculations of the BODC using Radau coordinates for H_2^{16}O , H_2^{18}O , and HD^{16}O . For the first two isotopomers, we only carry out calculations with the first HO bond length greater than the second, while for the last isotopomer, we do not make this restriction. We then solve for the F_α at each geometry, and fit them to the functional form

$$F_\alpha = \exp\{-\beta[(r_1 - r_e)^2 + (r_2 - r_e)^2]\} \sum_{ijk} c_{ijk}^\alpha [(r_1 - r_e)/r_e]^i [(r_2 - r_e)/r_e]^j [\cos(\theta) - \cos(\theta_e)]^k \quad (3)$$

and then use Eq.2 to evaluate the BODC for each isotopomer. We used the same values of β , r_e , and θ_e as in our previous work,[3] and included all terms with $i + j + k \leq 6$. It should be noted that β was erroneously described[3] as having the value $2 a_o^{-2}$. It actually has the value 2\AA^{-2} . The rms errors for the fits to F_α were 1.8×10^{-5} au and 7.7×10^{-5} au, resulting in rms errors in ΔV of less than 0.003 cm^{-1} . The linear coefficients c_{ijk}^α were determined by equally weighted least squares fits. Due to numerical errors, the fits did not quite have the desired symmetry, so the coefficients were symmetrized after the fitting.

IV. GENERALIZING THE HANDY METHOD

In this section we generalize the Handy method for the BODC to enable one to compute the non-adiabatic correction. We start first with the kinetic energy operator for the nuclei in an arbitrary space fixed frame:

$$T = -\frac{\hbar^2}{2} \sum_\alpha \frac{1}{m_\alpha} \sum_i \frac{\partial^2}{\partial X_{i\alpha}^2}, \quad (4)$$

where m_α is the mass of nuclei α , and i runs over cartesian components. We can re-write this in the form

$$T = \frac{\hbar^2}{2} \sum_{\alpha i} \left(\frac{\partial}{\partial X_{i\alpha}} \right)^\dagger \frac{1}{m_\alpha} \frac{\partial}{\partial X_{i\alpha}}, \quad (5)$$

where \dagger means complex conjugate acting to the left. Now we can compute the non-adiabatic correction functions as reported previously,[5] using the space fixed cartesian of Eq. 4. In this case one obtains the correction

$$\Delta T = \sum_{i\alpha j\alpha'} \left(\frac{\partial}{\partial X_{i\alpha}} \right)^\dagger C_{i\alpha j\alpha'}^{(2)} \frac{\partial}{\partial X_{j\alpha'}} + \sum_{i\alpha} \left[\left(\frac{\partial}{\partial X_{i\alpha}} \right)^\dagger C_{i\alpha}^{(1)*} + C_{i\alpha}^{(1)} \frac{\partial}{\partial X_{i\alpha}} \right] + C^{(0)}, \quad (6)$$

where

$$C_{i\alpha j\alpha'}^{(2)} = \sum_{n \neq 0} b_{i\alpha}^n \Delta_{0n}^{-1} b_{j\alpha'}^n, \quad (7)$$

$$C_{i\alpha}^{(1)} = \sum_{n \neq 0} b_{i\alpha}^n \left(\Delta_{0n}^{-1} b_0^n - \frac{1}{2} \mathcal{S}^n \right), \quad (8)$$

$$C^{(0)} = \sum_{n \neq 0} b_0^n \left(\Delta_{0n}^{-1} b_0^n - \mathcal{S}^n \right), \quad (9)$$

$$b_{i\alpha}^n = -\frac{\hbar^2}{m_\alpha} \langle \psi_n | \frac{\partial \psi_0}{\partial X_{i\alpha}} \rangle, \quad (10)$$

$$b_0^n = -\frac{\hbar^2}{2} \langle \psi_n | \sum_{i\alpha} \frac{1}{m_\alpha} \frac{\partial^2 \psi_0}{\partial X_{i\alpha}^2} \rangle, \quad (11)$$

$$\Delta_{0n} = W_0 - W_n, \quad (12)$$

and

$$\mathcal{S}^n = \Delta_{0n}^{-2} \sum_{i\alpha} b_{i\alpha}^n \frac{\partial W_0}{\partial X_{i\alpha}}, \quad (13)$$

where W_n is the Born-Oppenheimer energy of electronic state n , and ψ_n is the Born-Oppenheimer electronic wavefunction for electronic state n . When computing the derivatives, the origin used for the electronic wavefunctions is fixed. It should be noted that in general, the $C_{i\alpha j\alpha'}^{(2)}$, $C_{i\alpha}^{(1)}$, and $C^{(0)}$ are dependent on the geometry of the nuclei.

It will be convenient to express the coefficients in Eq.6 in terms of mass independent quantities. Now $m_\alpha m_{\alpha'} C_{i\alpha j\alpha'}^{(2)}$ is independent of mass, so that part is straightforward. For the other quantities, we need a partial decomposition, so that

$$C_{i\alpha}^{(1)} = \frac{1}{m_\alpha} \sum_{\alpha'} \frac{1}{m_{\alpha'}} C_{i\alpha\alpha'}^{(1)} \quad (14)$$

and

$$C^{(0)} = \sum_{\alpha\alpha'} \frac{1}{m_\alpha} \frac{1}{m_{\alpha'}} C_{\alpha\alpha'}^{(0)}. \quad (15)$$

The transformation from atomic cartesian to internal coordinates with total angular momentum eigenfunctions takes place in several steps. We now consider each step in turn.

A. Mass factor transformation

We next introduce the coordinate transformation

$$\mathbf{X} = \mathbf{x}\mathbf{M}, \quad (16)$$

where \mathbf{x} is the matrix of cartesian internal coordinates, and \mathbf{M} is a matrix of mass factors.[15–17] We assume that the final vector is for the center of mass, and \mathbf{M} is invertible. Let $\tilde{\mathbf{M}}$ denote the inverse of \mathbf{M} . Then since

$$\frac{\partial}{\partial X_{i\alpha}} = \sum_{\beta} \tilde{M}_{\alpha\beta} \frac{\partial}{\partial x_{i\beta}}, \quad (17)$$

where β indexes the internal coordinates, the kinetic energy operator becomes

$$T = \frac{\hbar^2}{2} \sum_{i\beta\beta'} \left(\frac{\partial}{\partial x_{i\beta}} \right)^\dagger \frac{1}{\mu_{\beta\beta'}} \frac{\partial}{\partial x_{i\beta'}}, \quad (18)$$

with

$$\frac{1}{\mu_{\beta\beta'}} = \sum_{\alpha} \tilde{M}_{\alpha\beta} \frac{1}{m_\alpha} \tilde{M}_{\alpha\beta'}. \quad (19)$$

It is easy to show that

$$\Delta T = \sum_{i\beta j\beta'} \left(\frac{\partial}{\partial x_{i\beta}} \right)^\dagger \tilde{C}_{i\beta j\beta'}^{(2)} \frac{\partial}{\partial x_{j\beta'}} + \sum_{i\beta} \left[\left(\frac{\partial}{\partial x_{i\beta}} \right)^\dagger \tilde{C}_{i\beta}^{(1)*} + \tilde{C}_{i\beta}^{(1)} \frac{\partial}{\partial x_{i\beta}} \right] + \tilde{C}^{(0)}, \quad (20)$$

with

$$\tilde{C}_{i\beta j\beta'}^{(2)} = \sum_{\alpha\alpha'} \tilde{M}_{\alpha\beta} C_{i\alpha j\alpha'}^{(2)} \tilde{M}_{\alpha'\beta'}, \quad (21)$$

$$\tilde{C}_{i\beta}^{(1)} = \sum_{\alpha} \tilde{M}_{\alpha\beta} C_{i\alpha}^{(1)}, \quad (22)$$

and

$$\tilde{C}^{(0)} = C^{(0)}. \quad (23)$$

B. Decouple Center of Mass

We next perform a transformation which takes the electronic coordinates and the coordinates for the nuclear center of mass and forms new coordinates consisting of the electronic coordinates with their origin the nuclear center of mass, and the coordinates for the total center of mass.[5] This transformation zeros the coupling between the center of mass and all other coordinates, and requires the inclusion of the mass polarization term[5] when computing matrix elements. Nevertheless, the numerical values of the matrix elements and the remaining correction functions are unchanged.

C. Euler internal

We next transform from the space fixed nuclear cartesian to body fixed coordinates defined by

$$\mathbf{x} = \mathbf{A}^T \mathbf{x}^{so}, \quad (24)$$

with \mathbf{A} a rotation matrix[17] parameterized by the Euler angles $\alpha\beta\gamma$, the superscript T denotes transpose, and \mathbf{x}^{so} the z embedding of Sutcliffe and Tennyson,[18] parameterized by the lengths r_1 and r_2 , the angle χ , and the embedding parameter a . The matrix \mathbf{A} can be easily determined by the relation

$$\mathbf{A} = \mathbf{V}(\mathbf{x}^{so})\mathbf{V}(\mathbf{x})^T, \quad (25)$$

where \mathbf{V} is a 3×3 orthogonal matrix constructed from the first two vectors of its argument. We take the first column of \mathbf{V} to be the unit vector parallel to the first vector of its argument, the third column to be the unit vector obtained by Schmidt orthogonalizing the first vector from the second, and the second column the cross product of the other two columns.

Then we introduce[19]

$$\frac{\partial}{\partial x_{i\beta}} = \sum_j A_{ji}(\alpha, \beta, \gamma) \sum_l g_{j\beta l} \hat{O}_l. \quad (26)$$

with \hat{O}_l and $g_{k\beta l}$ given in Table I. The coordinates l consist of the radial coordinates r_1 and r_2 , the bending angle χ , and the nuclear angular momentum operators R_ξ . In the table, R_ξ is the ξ component in the nuclear body-fixed frame of reference of the total nuclear angular

momentum, with its sign reversed to satisfy normal commutation relations. Substituting Eq. 26 into Eq. 18 easily yields the desired kinetic energy operator:

$$T = \frac{\hbar^2}{2} \sum_{l'} \hat{O}_l^\dagger G_{ll'} \hat{O}_{l'}, \quad (27)$$

with

$$G_{ll'} = \sum_{\beta\beta'k} g_{k\beta l}^* \frac{1}{\mu_{\beta\beta'}} g_{k\beta' l'}. \quad (28)$$

We must also remember to include the volume element obtained from the Jacobian determinant when computing matrix elements over vibrational-rotational functions. This volume element is not to be acted on by any of the \hat{O}_l when T is written as in Eq. 27. We can also write Eq. 27 in the more conventional form

$$T = \frac{\hbar^2}{2} \sum_{l'} \tilde{G}_{ll'} \hat{O}_l \hat{O}_{l'}. \quad (29)$$

As before, we obtain the non-adiabatic correction

$$\Delta T = \sum_{l'} \hat{O}_l^\dagger \tilde{\underline{C}}_{ll'}^{(2)} \hat{O}_{l'} + \sum_l \left[\hat{O}_l^\dagger \tilde{\underline{C}}_l^{(1)*} + \tilde{\underline{C}}_l^{(1)} \hat{O}_l \right] + \tilde{\underline{C}}^{(0)}, \quad (30)$$

with

$$\tilde{\underline{C}}_{ll'}^{(2)} = \sum_{kk'\beta\beta'} g_{k\beta l}^* \sum_{ij} A_{ki} \tilde{C}_{i\beta j\beta'}^{(2)} A_{k'j} g_{k'\beta' l'}, \quad (31)$$

$$\tilde{\underline{C}}_l^{(1)} = \sum_{k\beta} g_{k\beta l} \sum_i A_{ki} \tilde{C}_{i\beta}^{(1)}, \quad (32)$$

and

$$\tilde{\underline{C}}^{(0)} = \tilde{C}^{(0)}. \quad (33)$$

D. Rotational invariance

Finally, we fix the electronic positions with respect to the nuclear body-fixed axis. This results in the elimination of the nuclear angular momentum operator via the relation

$$R_\xi = J_\xi + L_\xi, \quad (34)$$

where ξ specifies the cartesian component in the nuclear body-fixed frame of reference, R is the nuclear angular momentum with sign reversed to satisfy normal commutation relations, J is the total angular momentum with sign reversed to satisfy normal commutation

relations, and L is the electronic angular momentum. Since the electronic wavefunction rotates with the molecule, J_ξ will have no effect on the electronic wavefunctions, thus matrix elements which were computed as derivatives with respect to the Euler angles are now computed as matrix elements of L_ξ , but the numerical values are unchanged.

E. Wavefunction Factorization

So far we have presented results where the radial coordinates have volume elements $r_i^2 dr_i$. It is convenient to introduce the factorization $\Psi_\eta = \Phi_\eta / (r_1 r_2)$ and solve for Φ_η rather than for Ψ_η . This changes some of the coefficients in Eq. 30. Specifically $\underline{\tilde{C}}^{(0)}$ is replaced with

$$\underline{\tilde{C}}^{(0)} = 2\underline{\tilde{C}}_1^{(1)} / r_1 - 2\underline{\tilde{C}}_2^{(1)} / r_2 + \underline{\tilde{C}}_{11}^{(2)} / r_1^2 + \underline{\tilde{C}}_{22}^{(2)} / r_2^2 + 2\underline{\tilde{C}}_{12}^{(2)} / r_1 r_2 \quad (35)$$

and then $\underline{\tilde{C}}_l^{(1)}$ is replaced by

$$\underline{\tilde{C}}_l^{(1)} = \underline{\tilde{C}}_{l1}^{(2)} / r_1 - \underline{\tilde{C}}_{l2}^{(2)} / r_2. \quad (36)$$

F. Summary

In summary, one computes $m_\alpha m_{\alpha'} C_{i\alpha j\alpha'}^{(2)}$, $C_{i\alpha\alpha'}^{(1)}$, $C_{\alpha\alpha'}^{(0)}$ using the appropriate modifications of Eqs. 7,8,9 on a grid. Then for a particular isotope, one forms $C_{i\alpha j\alpha'}^{(2)}$, $C_{i\alpha\alpha'}^{(1)}$, and $C_{\alpha\alpha'}^{(0)}$ (Eq. 14,15), then applies the mass transformation of Eqs. 21 and 22, then the rotation and coordinate transformation of Eqs. 31 and 32, and finally the factorization transformation of Eqs. 35 and 36. One could attempt to fit $m_\alpha m_{\alpha'} C_{i\alpha j\alpha'}^{(2)}$ etc directly, but since these quantities depend on the choice of origin, it is not clear what functional form to use. For this part of the calculation, we fit the $\underline{\tilde{C}}_{ll'}^{(2)}$, $\underline{\tilde{C}}_l^{(1)}$ and $\underline{\tilde{C}}^{(0)}$ calculated at 366 geometries with 165 parameters to a functional form like the one described previously.[5]

V. RESULTS

Now that we have the icMRCI BODC, we can test how well the BODC computed using the CASSCF wavefunction[5] is converged. In Table II we give our results obtained using the SCF BODC, the CASSCF BODC, and our new icMRCI BODC. All calculations used the cc-pVTZ basis.[20] These calculations use the un-optimized PES V^{5Z} as in Ref.5. To be consistent with our previous work,[5] we label the vibrational levels with local mode

quantum numbers. We see that we obtain quite similar results from all methods for bending overtones, but much larger differences for stretching overtones. The corrections obtained from the CASSCF method are overestimates for the stretches, for the icMRCI results always move toward the SCF results. Nonetheless, the SCF results are not reliable for stretches.

We now turn to our results using the new PES. In Table III, we give the errors for low lying levels of the various isotopomers from three different calculations: the results labeled V^{mass} are taken from Ref.[3] and are obtained using the empirical mass dependent correction, the results labeled BODC use the PES V^{emp} from Ref.[3] and the icMRCI BODC from the present work, and finally the results labeled Noad use the newly optimized PES V^{nemp} and include the icMRCI BODC and the non-adiabatic corrections. Since the PES did not include the BODC in its optimization, we subtract the $H_2\ ^{16}O$ BODC from the BODC computed for the isotopomer of interest. In this table, the levels are labeled by normal mode quantum numbers. Comparing the results from BODC and Noad, we see that in all cases but one, the Noad results are an improvement over the BODC results, and in some cases significantly so. The exception is the HO stretch in HTO, but both calculations do quite well for this level.

We can see how close we are to our goal of accurate *ab initio* predictions of isotopic shifts by comparing the errors to the average errors obtained for $H_2\ ^{16}O$, which was used to optimize the PES. The rms errors for the $H_2\ ^{16}O$ levels in Table III is 0.04 cm^{-1} . There are five errors larger than this in the table for the other isotopomers. Of the five, three are for the anti-symmetric stretch of $D_2\ ^{16}O$, $T_2\ ^{16}O$, and HO stretch of $HT\ ^{16}O$, and the largest is -0.10 cm^{-1} . These are probably not significantly larger than we expect. The remaining two are larger: 0.18 cm^{-1} for the symmetric stretch of $D_2\ ^{16}O$ and 0.22 cm^{-1} for the symmetric stretch of $T_2\ ^{16}O$. Since these errors are larger and are for the same mode, we think that these are real, significant, discrepancies. We are not sure of the origin of these differences, but we suspect that it is due to a deficiency in our calculations.

It is interesting to also compare our present best results to the previous ones using the empirical mass correction. In all but four cases, the empirical correction gives smaller errors. In these four cases, the errors are all small, except for the HO stretch in $HT\ ^{16}O$, where V^{mass} gives -0.14 cm^{-1} and our best *ab initio* results are -0.10 cm^{-1} . In contrast, in the two cases mentioned above where the *ab initio* calculations gave large errors, the empirical mass correction gives significantly smaller errors: 0.00 cm^{-1} and -0.11 cm^{-1} . However, on the whole, the two results are very similar, which is a very encouraging result.

VI. CONCLUSIONS

We have computed the isotopic shifts for the water molecule including both the diagonal and non-adiabatic corrections to the Born-Oppenheimer approximation. We find that both corrections are significant, and on the whole, the isotopic shifts are predicted quite well for low lying levels. The exceptions are the symmetric stretching fundamentals of $D_2^{16}O$ and $T_2^{16}O$, where the errors are about 0.2 cm^{-1} .

There are four possible sources of the disagreement: (i) the Born-Oppenheimer PES is not accurate enough, *i.e.* cancellation of errors allow most of the isotopomers to be fitted accurately, but not all, (ii) the BODC is not as accurate as we think — possible sources of error are the use of the cc-pVTZ basis and icMRCI wavefunctions, (iii) the non-adiabatic correction is not as accurate as we would like, either due to the inability of the scaling to make up deficiencies in the SCF/CIS method, the basis set is too small so that incorrect geometry dependence is obtained, or the fit is not good enough, or (iv) the experimental data is incorrect. Work is ongoing to test these possibilities. We are attempting to compute the best possible *ab initio* PES[21] as well as generalizing our non-adiabatic code to more accurate wavefunctions. Nonetheless, the future is very bright for accurate predictions of isotopic shifts.

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TABLE I: Coordinate transformation matrix.

$\frac{\partial}{\partial r_1}$	$\frac{\partial}{\partial r_2}$	$\frac{\partial}{\partial \chi}$	R_x	R_y	R_z
$-\sin a\chi$	0	$-\cos a\chi/r_1$	0	$(1-a)\cos a\chi/ir_1$	0
0	0	0	$-\sin(1-a)\chi/(ir_1 \sin \chi)$	0	$-\cos(1-a)\chi/(ir_1 \sin \chi)$
$\cos a\chi$	0	$-\sin a\chi/r_1$	0	$(1-a)\sin a\chi/ir_1$	0
0	$\sin(1-a)\chi$	$\cos(1-a)\chi/r_2$	0	$a\cos(1-a)\chi/ir_2$	0
0	0	0	$-\sin a\chi/(ir_2 \sin \chi)$	0	$\cos a\chi/(ir_2 \sin \chi)$
0	$\cos(1-a)\chi$	$-\sin(1-a)\chi/r_2$	0	$-a\sin(1-a)\chi/ir_2$	0

TABLE II: BODC for H₂O from various electronic wavefunctions (in cm⁻¹).

$\nu_b\nu_s$	SCF	CASSCF	icMRCI
0(0,0)+	0.00	0.00	0.00
1(0,0)+	-0.50	-0.46	-0.45
2(0,0)+	-1.00	-0.94	-0.91
0(1,0)+	-0.05	0.39	0.28
0(1,0)-	0.13	0.62	0.47
3(0,0)+	-1.52	-1.46	-1.40
1(1,0)+	-0.49	-0.01	-0.11
1(1,0)-	-0.31	0.24	0.09
4(0,0)+	-2.08	-2.03	-1.95
2(1,0)+	-0.94	-0.42	-0.50
2(0,1)-	-0.74	-0.16	-0.29
0(2,0)+	-0.05	0.96	0.67
0(2,0)-	0.09	1.19	0.83
0(1,1)+	0.21	1.22	0.90

TABLE III: Errors and experimental energies for low-lying vibrational levels of various isotopic substitutions (in cm^{-1}).

Source	H_2^{16}O	HD^{16}O	D_2^{16}O	T_2^{16}O	HT^{16}O
			010		
V^{mass}	-0.03	-0.04	-0.03	0.00	-0.01
BODC		0.02	0.00	-0.04	-0.04
Noad	0.05	0.01	0.00	-0.02	0.01
exp.	1594.78 ^a	1403.48 ^a	1178.38 ^b	995.33 ^c	1332.48 ^d
			020		
V^{mass}	0.00	-0.01	0.00		
BODC		0.20	0.06		
Noad	0.05	0.07	0.00		
exp.	3151.63 ^a	2782.01 ^a	2336.84 ^e		
			100		
V^{mass}	0.01	0.02	0.00	-0.11	-0.04
BODC		0.51	0.62	0.39	0.31
Noad	-0.04	0.00	0.18	0.22	0.03
exp.	3657.04 ^a	2723.68 ^a	2671.65 ^e	2237.15 ^f	2299.77 ^g
			001		
V^{mass}	-0.03	-0.01	-0.01	-0.01	-0.14
BODC		0.76	0.58	0.29	-0.07
Noad	0.03	0.02	-0.07	-0.08	-0.10
exp.	3755.96 ^a	3707.47 ^a	2787.72 ^e	2366.60 ^h	3716.58 ^f

^aRef.7

^bRef. 22

^cRef. 23

^dRef. 24

^eRef. 25

^fRef. 26

^gRef. 27

^hRef. 28